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INFRARED COATING STUDIES

FINAL REPORT

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## INTRODUCTION

Section I of this report represents a continuation of the survey of infrared reflectance. In particular, the effect of impurities on the infrared reflectance of pressed materials is observed. The second section reports some initial results of an investigation of the properties of  $\text{LiF}$  thin film chips. A brief summary of the activities pursued during this contract is included at the end of the report.

## SECTION I

### Continuation of the Survey of Infrared Reflectance

The infrared reflectance of 18 materials was measured at normal incidence over the wavelength interval 2-36 microns (Figs. 1-9). This is a continuation of the survey initiated in the Third Quarterly Report of 1961. The discussion of the spectrophotometric reproducibility and resolution in that report remains valid for the present data.

Samples of pressed materials ( $\text{ZrO}_2$ ,  $\text{BaTiO}_3$ ,  $\text{TiO}_2$ ) obtained from the Titanium Alloy Manufacturing Division of the National Lead Company made it possible to examine the effect of the addition of impurities on infrared reflectance. Previous measurements made on single crystals of  $\text{CaF}_2$  with concentrations of  $\text{U}^{+++}$  up

to 2.5 percent showed no change in reflectance. The high levels of doping in the pressed samples did effect the infrared reflectance. Generally, it was found that the reststrahlen reflectance decreased as the percentage doping increased.

There are several possible explanations for the impurity effect. The samples were pressed and a certain amount of scattering is possible. It is likely that any such scattering would depend on the impurity concentration. The impurities also result in new lattice vibrational modes that might be strong enough to appreciably change the infrared dispersion of the material. A third possible explanation is that the infrared dispersion seems to depend on crystallite size (Quarterly Report #1, 1962). It is likely that crystallite size is strongly influenced by doping. Only a much more detailed investigation would show what role these three mechanisms play in changing the reststrahlen reflectance. It is possible to make several tentative observations even on this incomplete data. First it is necessary to decide in what way these mechanisms would be expected to effect the reflectance.

- a. Scattering should decrease the reflectance in both the reststrahlen high reflectance band

and at shorter wavelengths. Scattering would be much more pronounced at short wavelengths dropping off as a high negative power of wavelength.

- b. Impurity vibrational modes would probably result in a reflectance change only in a limited wavelength range near the resonant frequency of the mode. The dispersion due to such a mode would generally be very weak, but it can be shown that the short wavelength edge of the reststrahlen high reflectance band is very sensitive to even weak dispersion terms.
- c. The effect of small crystallites would be to enhance anharmonic effects; i.e. to smooth out the high reflectance band with little change at short wavelengths and to make combination bands more pronounced.

The decrease in reflectance  $\text{TiO}_2$  (Fig. 3) at short wavelengths strongly indicates scattering. The change in reflectance of the  $\text{BaTiO}_3$  series (Fig. 4) over a large wavelength interval also suggests a scattering phenomenon. It is possible, though, that crystallite size may have some influence in smoothing out the high reflectance band. The change in reflectance of  $\text{ZrO}_2$  (Fig. 1 and 2) over only a limited wavelength interval

at the sensitive short wavelength edge of the high reflectance band, strongly points to the formation of an optically active impurity mode. This is not too surprising considering the high percentage of doping. Naturally, a crystallite size effect is impossible in glass and scattering effects in the infrared are improbable. Observation of impurity modes in glass is also improbable since there are no sensitive intrinsic high reflectance bands in the material to accentuate such modes. Figure 7 shows that glass with impurity concentrations up to 6 percent shows no measurable change in infrared reflectance.

The sample of PbS (Fig. 5) was a mineral and the polished surface was rather porous. The small peak at 9 microns may be due to quartz impurities.



## SECTION II

### Investigation of the Properties of LiF Thin Film Chips

The meaning of crystallite size in thin films as determined by, for example, X-ray line broadening or electron microscopy deserves more clarification. As described in Section III of the Third Quarter Report an experiment was devised to contribute to the solution of this problem. If the crystallite size in a thin film is restricted by the thickness dimension of the film it could be expected that optical measurements of film thickness should correlate with that part of the X-ray line broadening due to crystallite size. In this way we might be able to differentiate between size and strain broadening. Specifically, it was intended to use a sufficiently high substrate temperature for LiF films so that the crystallite size (at least as measured for thick LiF films) would greatly exceed the film thickness. Thus LiF films deposited at 300°C appear to have a crystallite size of the order of 15,000Å. If such films were made only 500Å thick it might be expected that X-ray line broadening would yield this thickness, if there were no strain broadening. The existence of a simple correlation between optical thickness measurements and X-ray broadening in a thin film assumes that crystallite size is

independent of film thickness under the above conditions. In view of a remark by L.G. Schulz (J. Chem. Phys., 17, 1153-1162, 1949) this may not be the case. He states that the relation between crystallite size and film thickness, for LiF film deposited at room temperature, is a nearly linear one. In a 500A thick film he found a crystallite size of 50A.

Despite this complication the experiment was begun. What information it would yield, and some preliminary results are noted in the following. Films of LiF thin enough to artificially restrict crystallite size to dimensions amenable to X-ray line broadening determinations are too thin to give a satisfactory response on the diffractometer. Accordingly the films are made to the desired thickness and removed from the glass substrate as small flakes or chips. This material is then compacted to a depth sufficient for the X-ray work.

In order to obtain a large number of chips in a single evaporation, a large substrate area is needed. The substrate used in this experiment is a hemispherical glass bowl seven inches in diameter. The source was placed in a position that gave a uniform coating over the entire hemisphere. The substrate temperature could be varied from 25-300°C.

To facilitate the removal of the LiF, a thin layer (500-1000Å) of zinc sulfide was evaporated first. The zinc sulfide was fired from a howitzer at a pressure of  $10^{-4}$  Torr.

First a series of LiF films with an optical thickness of  $0.6\mu$  was made at various substrate temperatures. The LiF was fired from a tantalum boat at an average pressure of  $5 \times 10^{-5}$  Torr. It was found that at high temperatures ( $200-300^{\circ}\text{C}$ ) the films could not be removed from the substrate. The thicker the film, however, the more readily it could be removed. The procedure for removing the film was to wash the substrate with water and/or acetone, collecting the chips in a filter paper. In view of the difficulties with these very thin chips some work with thicker ones was interjected.

A series of  $8\mu$  thick chips was made at 25, 130, and  $270^{\circ}\text{C}$ . These will be sedimented onto a new substrate and the X-ray diffraction pattern and reststrahlen will be measured and compared with the same measurements of the original films. Some chips have been sedimented onto glass and the X-ray diffraction patterns show that the chips have the same preferred orientation as the original films. This is to be expected since the chips are flat and would tend to settle in a direction parallel to the surface of the new substrate.

#### CONTRACT SUMMARY

A study was made of the effect of crystallite size on the infrared dispersion of LiF thin films. The infrared reststrahlen reflectance and the crystallite size of evaporated thin films of LiF were found to increase with increasing substrate temperature during evaporation. The change in reflectance appeared to be due to a change in the optical constants of LiF. The index of refraction of the films was calculated from reflectance measurements using the Drude dispersion relation. The data was compared with the theoretical work of H.B. Rosenstock.

The dependence of crystallite size of LiF thin films on the temperature of the substrate during evaporation was studied. An electron microscope was used to examine carbon replicas of the film surfaces. The mean dimension of the crystallites seemed to vary from 1000-5000A for 6 micron films deposited at room temperature to at least 15,000A for films evaporated at 300°C. It was suggested that the problem of film structure might be further enlightened by the investigation of chips of LiF films. Such samples might have the desirable properties of both thin films and bulk material. Work was begun in this direction.

An explanation of the preferred crystallographic

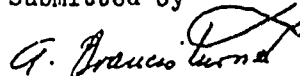
orientation of thin films deposited on amorphous substrates was presented. It was concluded that at high substrate temperatures and low rates of evaporation planes with low surface energy will be preferred, and at low substrate temperatures and high rates of evaporation high surface energy will be preferred.

It was shown that this is in good agreement with the preferred orientations observed in germanium films.

The survey of infrared reflectance, reststrahlen in particular, initiated in the 1961 contract was continued. The following table is a cumulative index of the materials examined in both contracts.

This report was prepared by T.P. Martin, J.D. Masso and A.F. Turner

Submitted by



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Material Research & Development

CUMULATIVE INFRARED REFLECTANCE INDEX

1961 - Contract DA-44-009 ENGL686

1962 - Contract DA-44-009 ENGL954

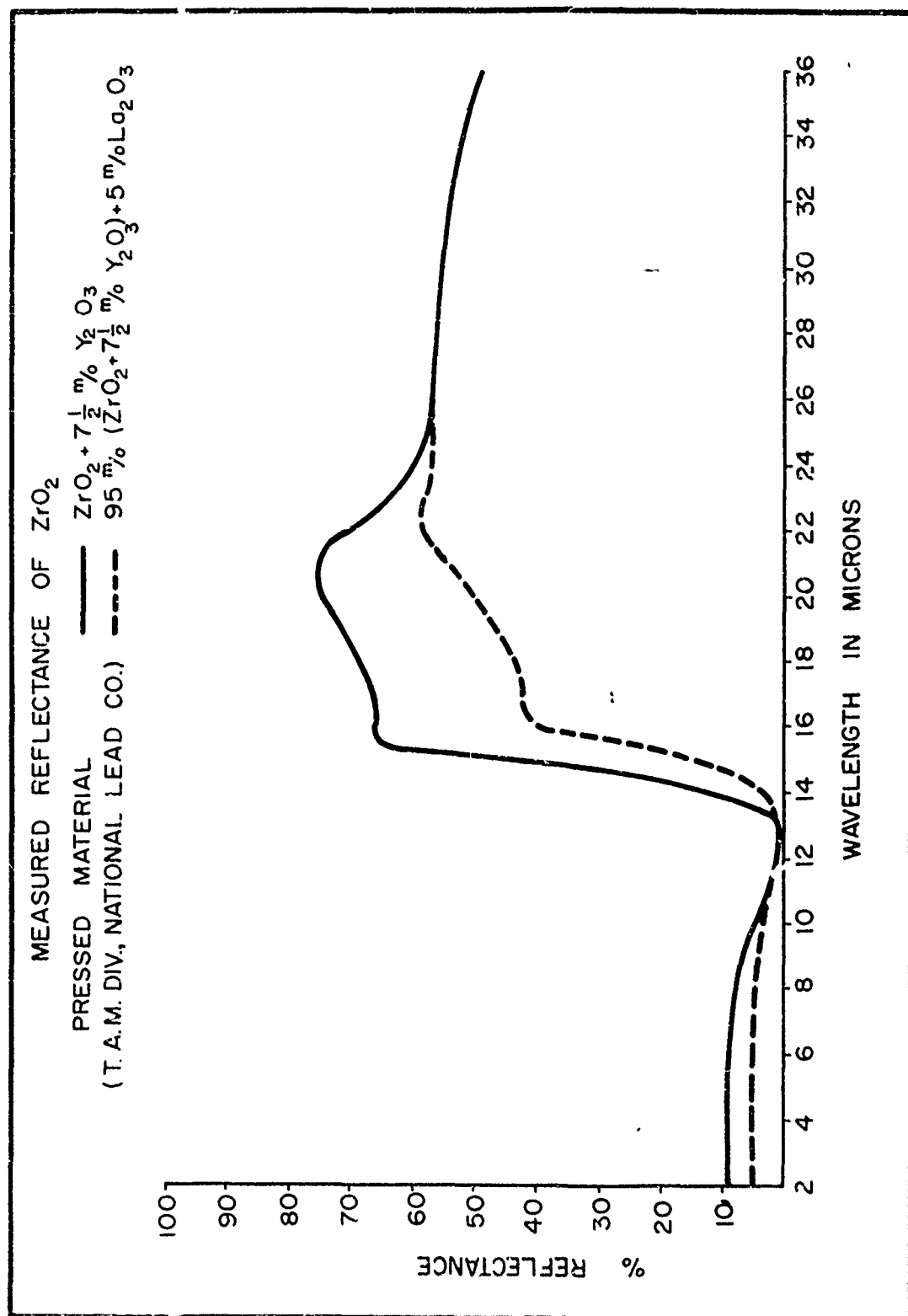
<u>MATERIAL</u>	<u>FORM</u>	<u>QUARTERLY REPORT</u>	<u><math>\lambda</math> in <math>\mu</math></u>	<u>FIG</u>
A Shiny Stone	Mineral	IV 1962	2 - 36	9
Barium Fluoride BaF <sub>2</sub>	Crystal	II 1961	14 - 36	1
	Crystal	III 1961	14 - 36	5
	Pressed	IV 1961	14 - 36	4
Barium Titanate BaTiO <sub>3</sub>	Pressed	IV 1962	2 - 36	4
+0.3m/0 La	Pressed	IV 1962	2 - 36	4
Bismuth Selenide Bi <sub>2</sub> Se	Crystal	IV 1961	14 - 36	10
		III 1962	4 - 36	10
Bismuth Telluride BiTe	Crystal	IV 1961	14 - 36	10
Boron Nitride BN	Pressed	V 1962	2 - 36	6
Calcium Fluoride CaF <sub>2</sub>	Crystal	III 1961	14 - 36	2-4
Cassiterite SnO <sub>2</sub>	Mineral	III 1962	4 - 36	4
Chert SiO <sub>2</sub>	Mineral	III 1962	4 - 36	7
Chiolite 5NaF.3AlF <sub>3</sub>	Crystal	III 1962	4 - 36	3

<u>MATERIAL</u>	<u>FORM</u>	<u>QUARTERLY REPORT</u>	<u><math>\lambda</math> in <math>\mu</math></u>	<u>FIG</u>
Cryolite $3\text{NaF} \cdot \text{AlF}_3$	Crystal	I 1962 III 1962	14 - 36 4 - 36	15 3
Galena PbS	Mineral	IV 1962	2 - 36	5
Gallium Arsenide GaAs	Crystal	I 1962	14 - 36	13
Garnet	Mineral	III 1962	4 - 36	6
Germanium Ge	Crystal	IV 1961	14 - 36	9
Glasses				
EDF-2	B&L	IV 1961	14 - 36	7
Irtran - II	E.K.	IV 1961	14 - 36	6
IR - 2 (Silicate)	B&L	III 1962	4 - 36	12
IR - 20 (Germanate)	B&L	III 1962	4 - 36	12
Arsenic Trisulfide		IV 1961	14 - 36	8
Glass				
+2% Nd	B&L	IV 1962	2 - 36	7
+6% Nd	B&L	IV 1962	2 - 36	7
+2% $\text{SmO}_3$	B&L	IV 1962	2 - 36	7
+2% $\text{Dy}_2\text{O}_3$	B&L	III 1961	14 - 36	6
Quartz				
Graphite C	Pressed	IV 1961	14 - 36	9
Labradorite	Mineral	III 1962	4 - 36	5
Lead Telluride PbTe	Crystal	IV 1961	14 - 36	10

<u>MATERIAL</u>	<u>FORM</u>	<u>QUARTERLY REPORT</u>	<u>Slide</u>	<u>Fig</u>
Lithium Fluoride LiF	Crystal Thin Film	IV 1961 I 1962	14 - 36 14 - 36	1 A,B 5
Magnesium Fluoride $MgF_2$	Pressed	III 1961	14 - 36	7
Magnesium Oxide $MgO$	Crystal	III 1961	14 - 36	8
Molybdenum Disilicide $MoSi_2$	Pressed	III 1962	4 - 36	11
Moonstone	Mineral	IV 1962	2 - 36	8
Nickel Sulfate $NiSO_4$	Crystal	III 1962	4 - 36	1
Petrified wood	Mineral	III 1962	4 - 36	9
Potassium Dihydrogen Orthophosphate $KH_2PO_4$	Crystal	III 1962	4 - 36	2
Quartz $SiO_2$	Crystal	IV 1961	14 - 36	3
Sapphire $Al_2O_3$	Crystal	IV 1961	14 - 36	2
Silicon Si	Crystal	IV 1961	14 - 36	9
Strontium Fluoride $SrF_2$	Pressed	IV 1961	14 - 36	5
Strontium Titanate $SrTiO_3$	Crystal	I 1962	14 - 36	16
Tiger's Eye	Mineral	III 1962	14 - 36	8



<u>MATERIAL</u>	<u>FORM</u>	<u>QUARTERLY REPORT</u>	<u><math>\lambda</math> in <math>\mu</math></u>	<u>FIG</u>
Titanium Dioxide TiO <sub>2</sub> + 1m/o Rb <sub>2</sub> O <sub>5</sub>	Crystal Pressed Pressed	IV 1962 IV 1962 IV 1962	2 - 36 2 - 36 2 - 36	3 3 3
Zinc Sulfide ZnS	Crystal	I 1962	14 - 36	14
Zirconium Oxide ZrO <sub>2</sub> + 7 1/2 m/o Y <sub>2</sub> O <sub>3</sub> above + 5 m/o La <sub>2</sub> O <sub>3</sub> +17 m/o CaO +15 m/o CaO above + 2 m/o La <sub>2</sub> O <sub>3</sub>	Pressed Pressed Pressed Pressed Pressed	IV 1962 IV 1962 IV 1962 IV 1962 IV 1962	2 - 36 2 - 36 2 - 36 2 - 36 2 - 36	1 1 2 2 2



MEASURED REFLECTANCE OF  $ZrO_2$   
 PRESSED MATERIAL  
 (T.A.M. DIV., NATIONAL LEAD CO.)

- $ZrO_2 + 17^m\%$   $CeO_2$  (TETRAGONAL)
- $ZrO_2 + 15^m\%$   $CaO_2$  (CUBIC)
- $ZrO_2 + 15^m\%$   $CaO_2 + 2^m\%$   $La_2O_3$  (CUBIC)

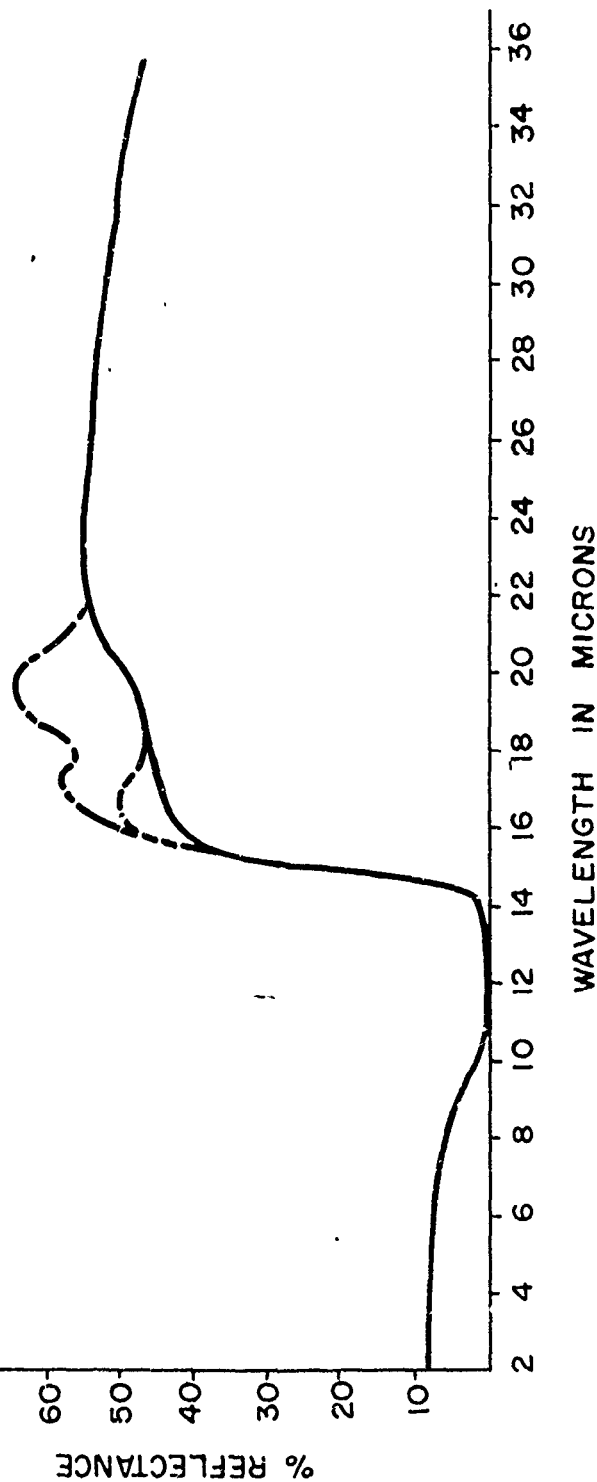


FIG. 2

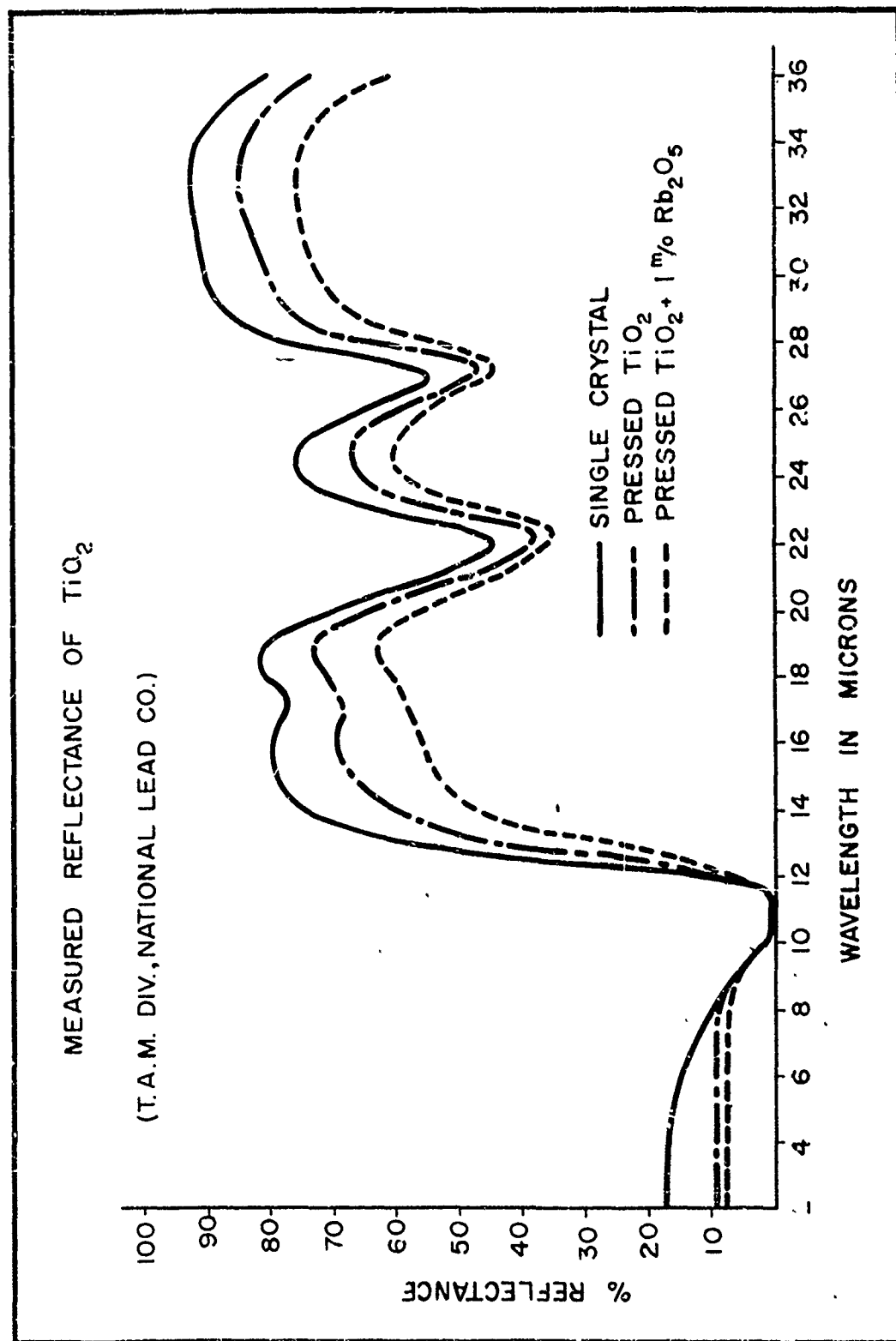


FIG. 3

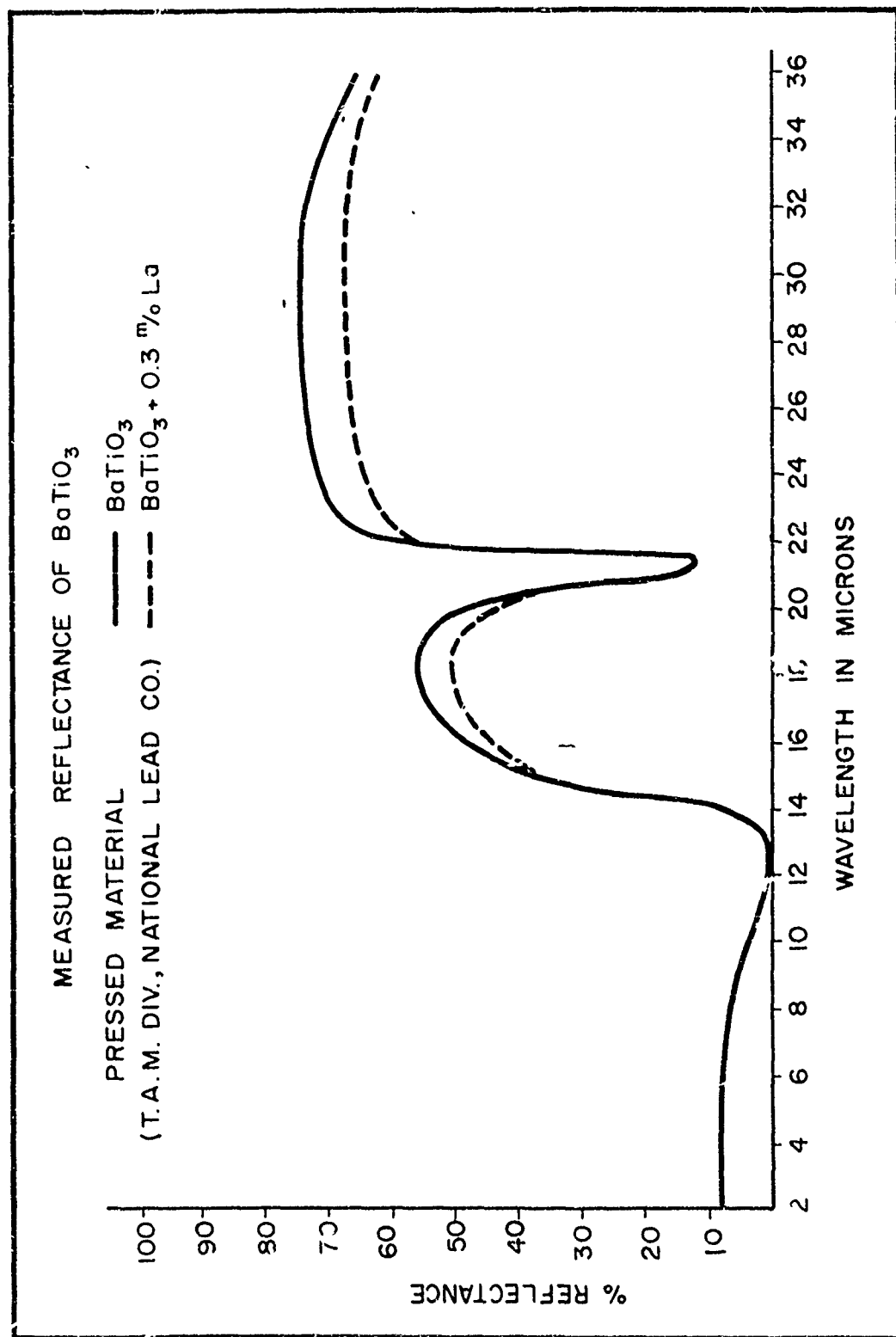


FIG. 4

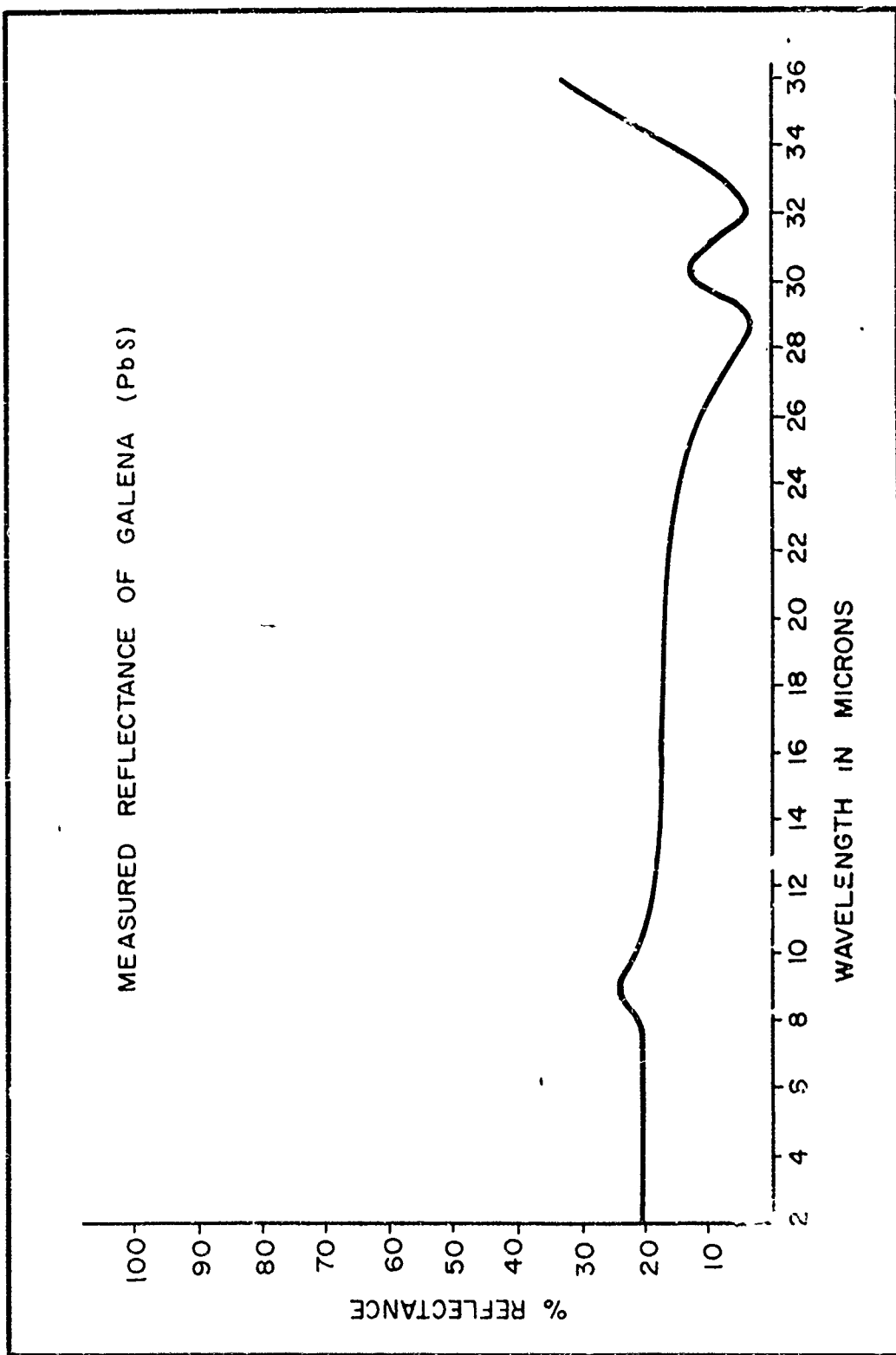


FIG. 5

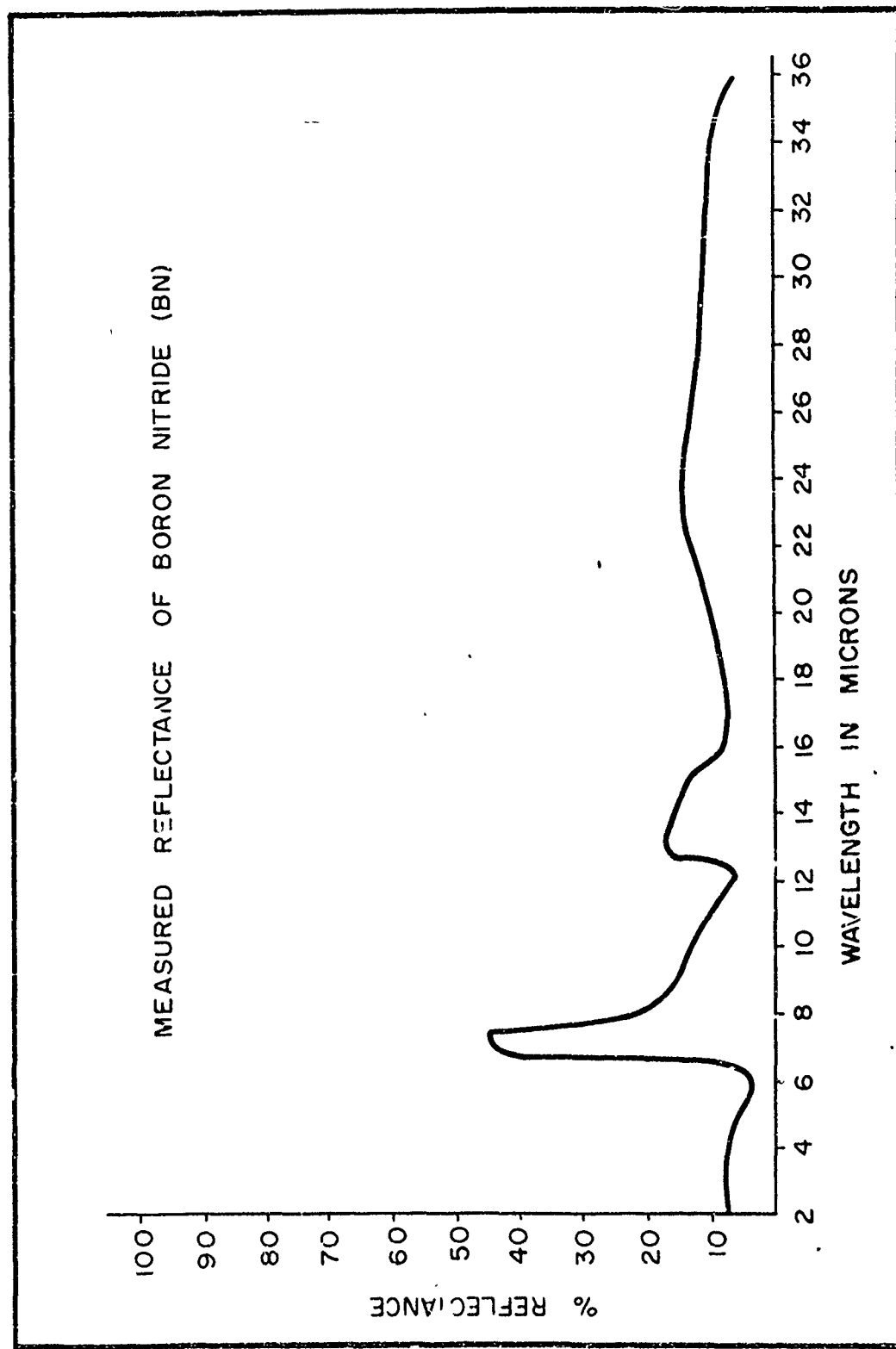


FIG. 6

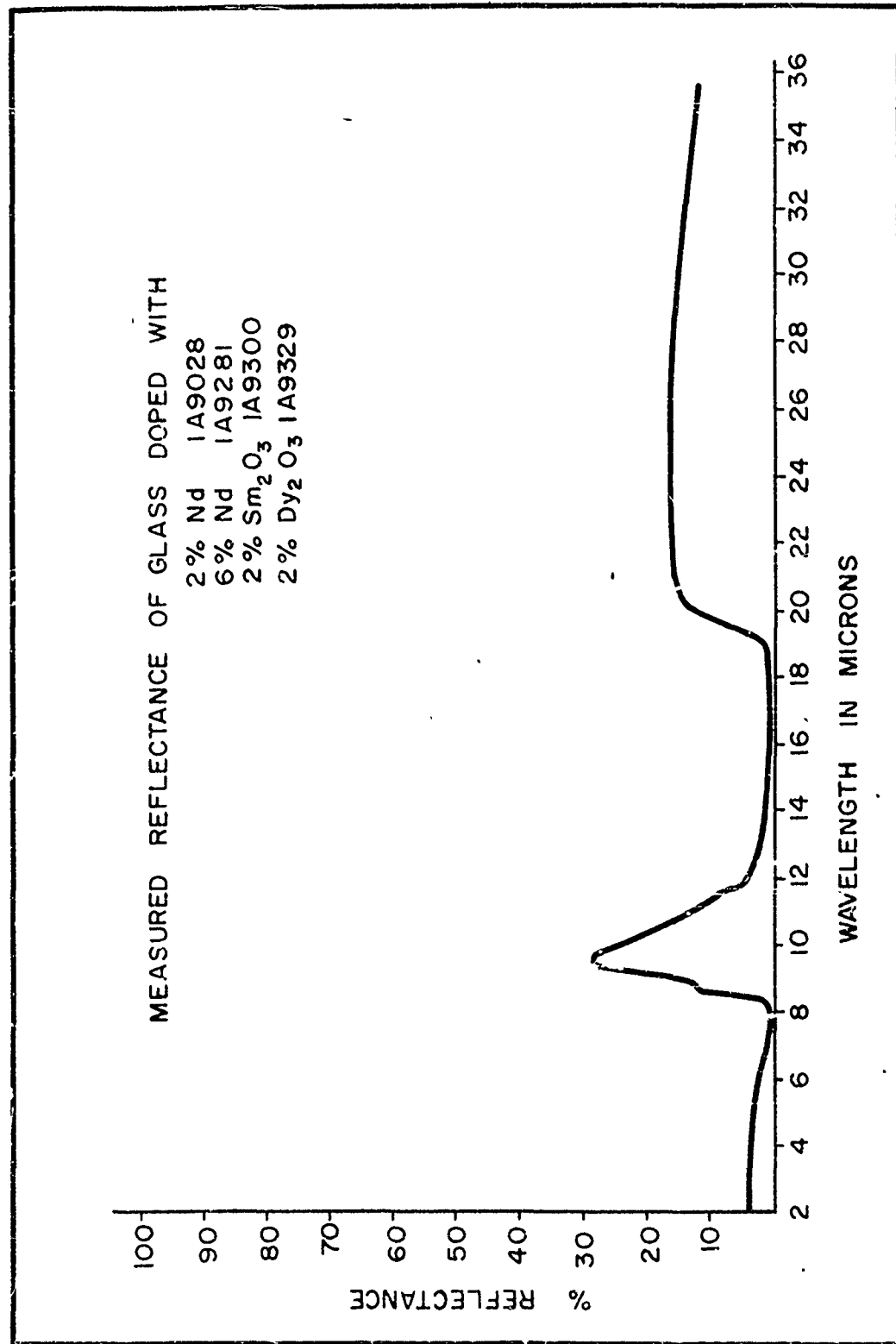


FIG. 7



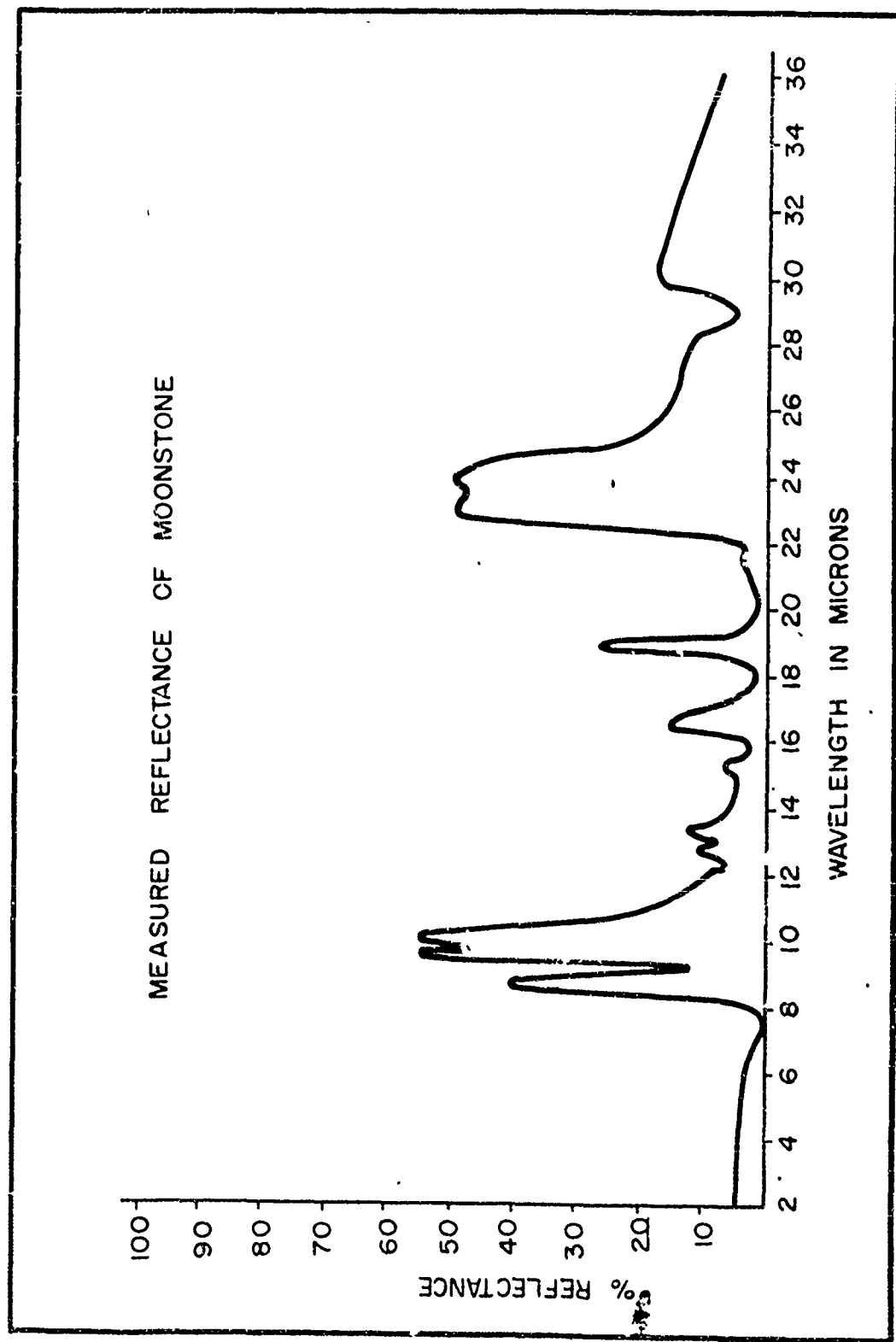


FIG. 8

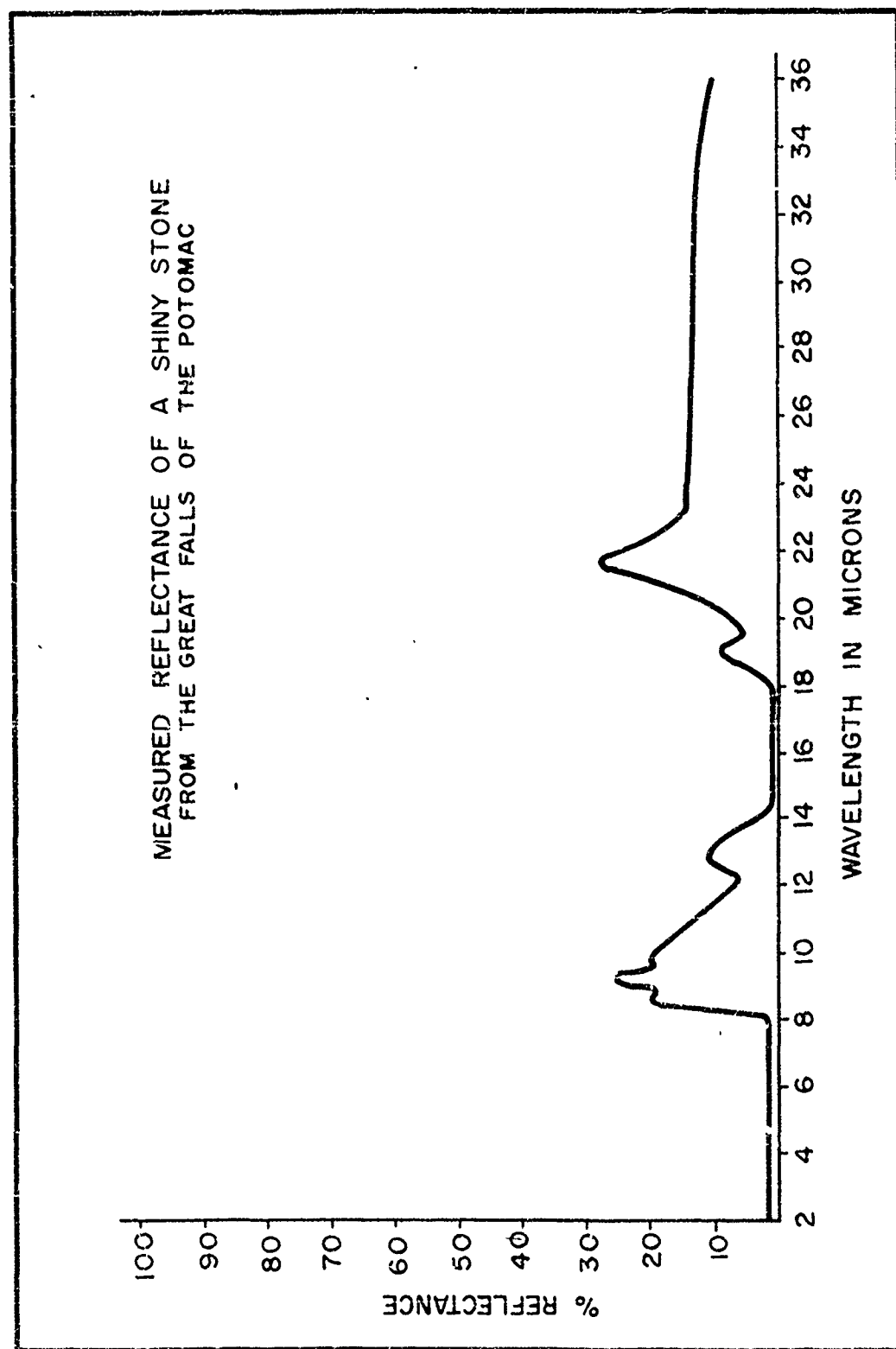


FIG. 9

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